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Tailoring hierarchically structured SiO_2 spheres for high pressure CO_2 adsorption

Supporting information

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Elemental Analysis

C, H, N Elemental Analysis

The C, H and N content of SiO_2 spheres were determined with a EURO EA elemental analyzer. 1-2 mg of each sample was weighed in a tin beaker. The samples were burned at 1000 °C in a He stream. After the reduction of NO_x compounds, the gas stream was separated with a GC column. The products (CO_2, NO_2, H_2O) were analyzed with a thermal conductivity detector (TCD).

Zr Elemental Analysis

50 mg of each sample was digested in a solution of 2 ml deionized water, 2 ml HF and 0.5 ml of H_2SO_4. Sc_2O_3 was added as an internal standard. The acid digestion was conducted in a pressure resistant vessel at 85 °C until a clear solution was obtained. The Zr content was determined with inductively coupled plasma optical emission spectrometry (ICP OES). A $ZrClO_2$/HCl solution was used as an internal standard.

Synthesis of SBA-15

6 g of hydrochloric acid (Sigma Aldrich, 37 wt.%) was added to 188.5 g of DI water and 10.25 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, BASF, M_w of 5750 Da) under rigid stirring. The solution was stirred for 1 day at 35 °C until a homogenous phase was obtained. After 2 h tetraethylorthosilicate (TEOS, Sigma Aldrich, purity ≥ 99 %) was added to the solution and the mixture was stirred at 35 °C for additional 24 h. The polymerized solution was aged in autoclaves at 80 °C for 24 h. The solution was filtered with deionized water 3 times and the precipitate was dried at 60 °C for 5 h prior to calcination in synthetic air (8 h at 600 °C, heating rate: 2.5 K/min, total flow rate: 100 ml/min).

Reactor column

The mixed precursor solution was injected directly into the injection flow on top of the reactor column (Figure S 1). The temperature of the reactor column was constant at 65 °C. The precursor solution was injected with a syringe pump at a flow rate of 15 ml·h^{-1}. The main flow in the column was 7 l·h^{-1} and the injection flow was 2 l·h^{-1}. Both flows have to be adjusted to the density of the Si^{4+} precursor solution in order to assure the sinking of the spheres to the bottom of the reactor. The length of the reactor column is 4 m.

The equilibrium constant (K) was determined via the Langmuir adsorption isotherm:

$$\frac{\theta(p)}{\theta_{max}} = \frac{K \cdot p}{1 + K \cdot p}$$

The equilibrium constant K was determined from the pressure dependency of the coverage θ (p) and the saturation coverage θ_{max}. Using values of K at two different temperatures the standard heat of adsorption ΔH^0 and standard entropy of adsorption ΔS^0 were calculated from the standard Gibb's free enthalpy ΔG^0.

$$\Delta G = \Delta G^0 + R \cdot T \cdot \ln(K) = 0$$

$$\Delta G^0 = -R \cdot T \cdot \ln(K)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -R \cdot T \cdot \ln(K)$$

$$K = e^{\frac{\Delta S^0}{R}} \cdot e^{-\frac{\Delta H^0}{RT}}$$

Supporting figures

Figure S 1 Flow sheet of the reactor column for synthesis of millimeter-scaled SiO_2 spheres.

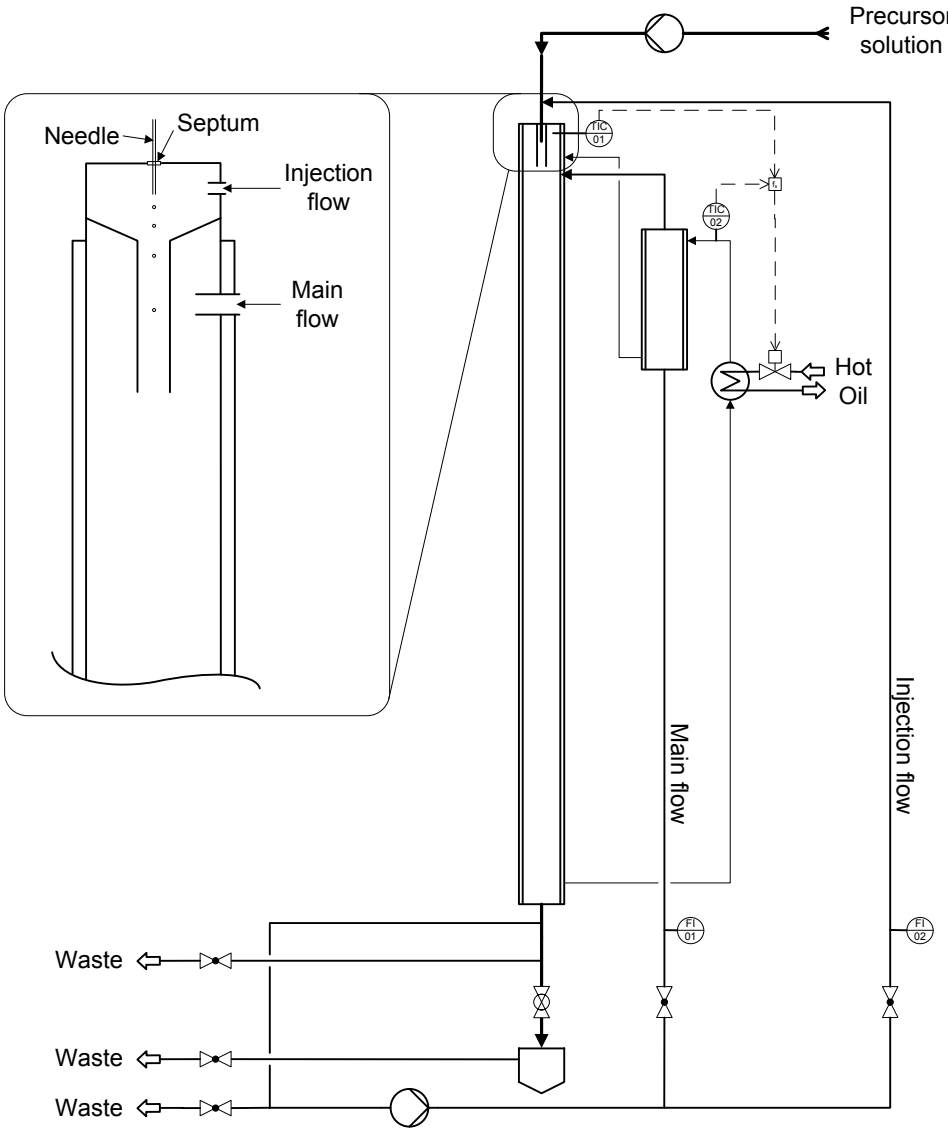


Figure S 2 Flow sheet of the high-pressure magnetic suspension balance (Rubotherm).

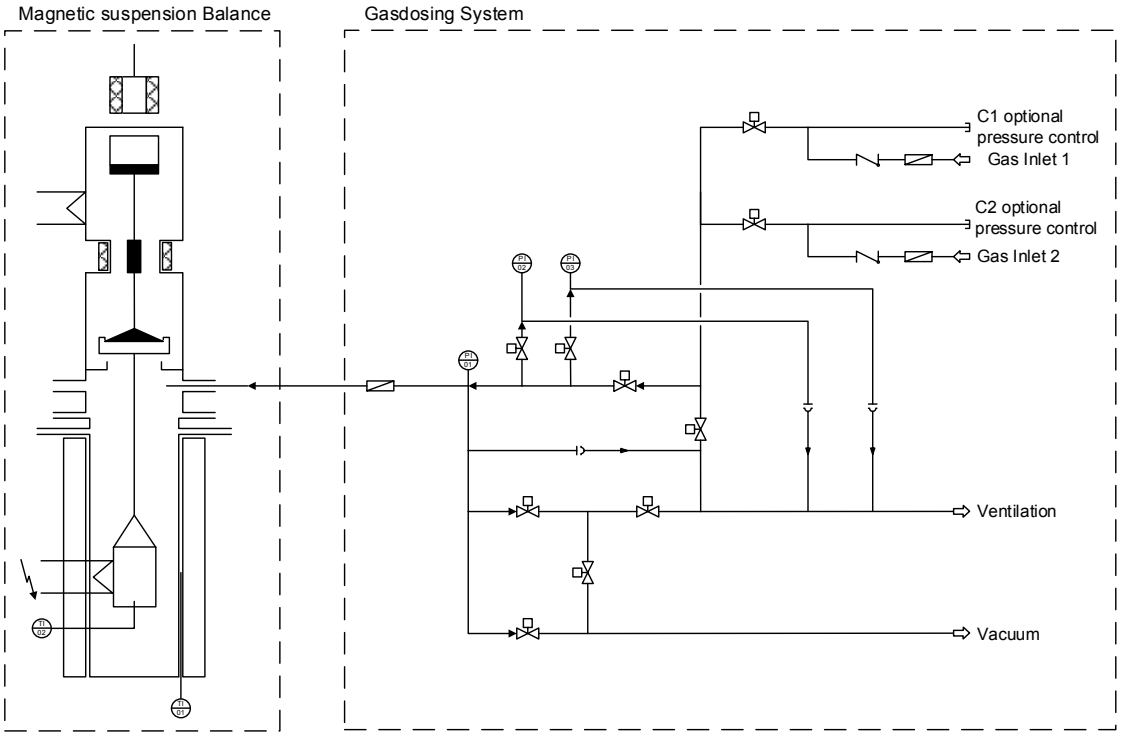


Figure S 3 N_2 adsorption (filled symbol) and desorption (unfilled symbol) isotherms of (a, b) aniline, (c, d) benzyl alcohol and (e, f) butanol spheres. Isotherms are vertically shifted in steps of 200 $cm^3 \cdot g^{-1}$ for (a, c, e) as prepared and in steps of 400 $cm^3 \cdot g^{-1}$ for (b, d, f) calcined SiO_2 spheres. 0 (I) , 1 (II) and 7 (III) wt.% Zr^{4+}.

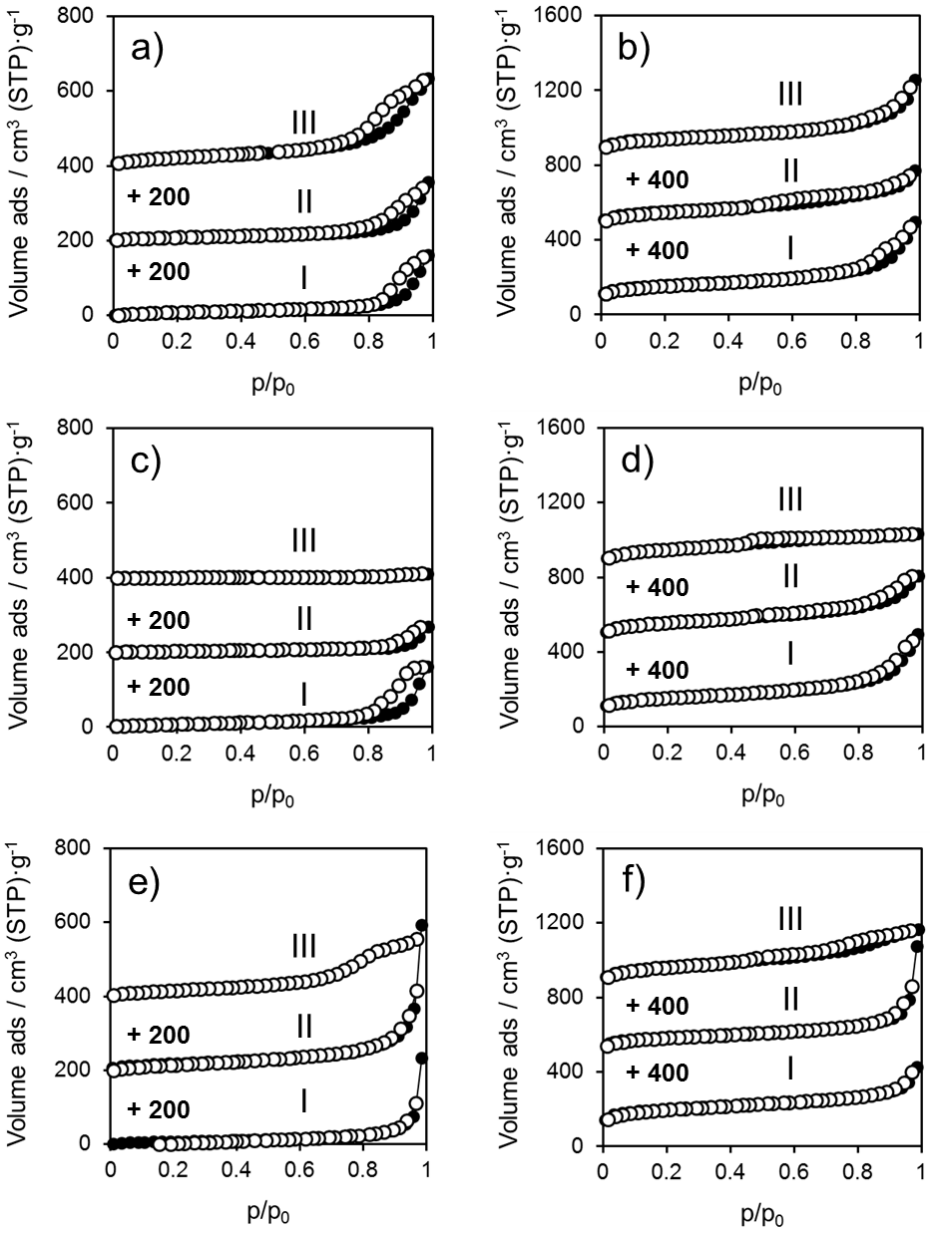


Figure S 4 N_2 physisorption isotherms of (a) SBA-15 and (c) zeolite 13X. Filled and empty symbols represent adsorption and desorption branches, respectively. Pore size distribution of (b) SBA-15 and (d) zeolite 13X calculated by BJH method (N_2 desorption branch) and (d) additionally DA method for micropore analysis.

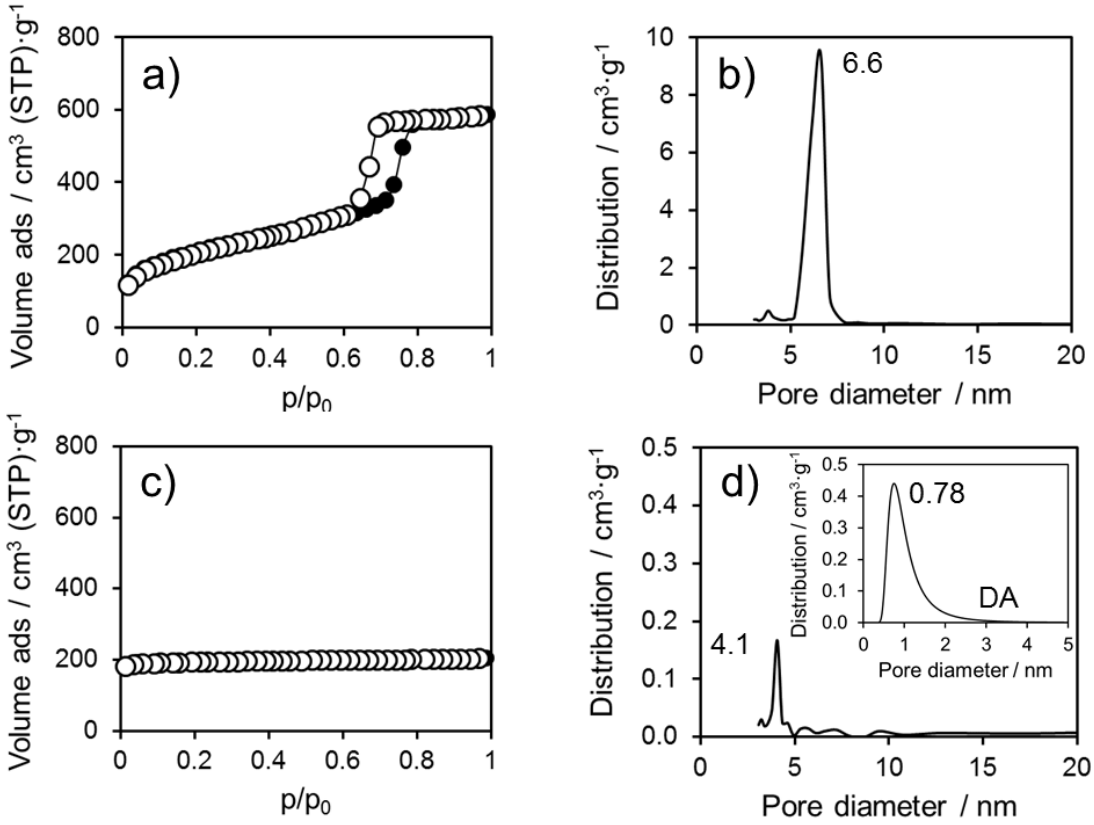


Figure S 5 XRD of t-ZrO_2, (a) aniline, (b) butanol and (c) benzyl alcohol Zr(0) (I) , Zr(1) (II) and Zr(7) (III).

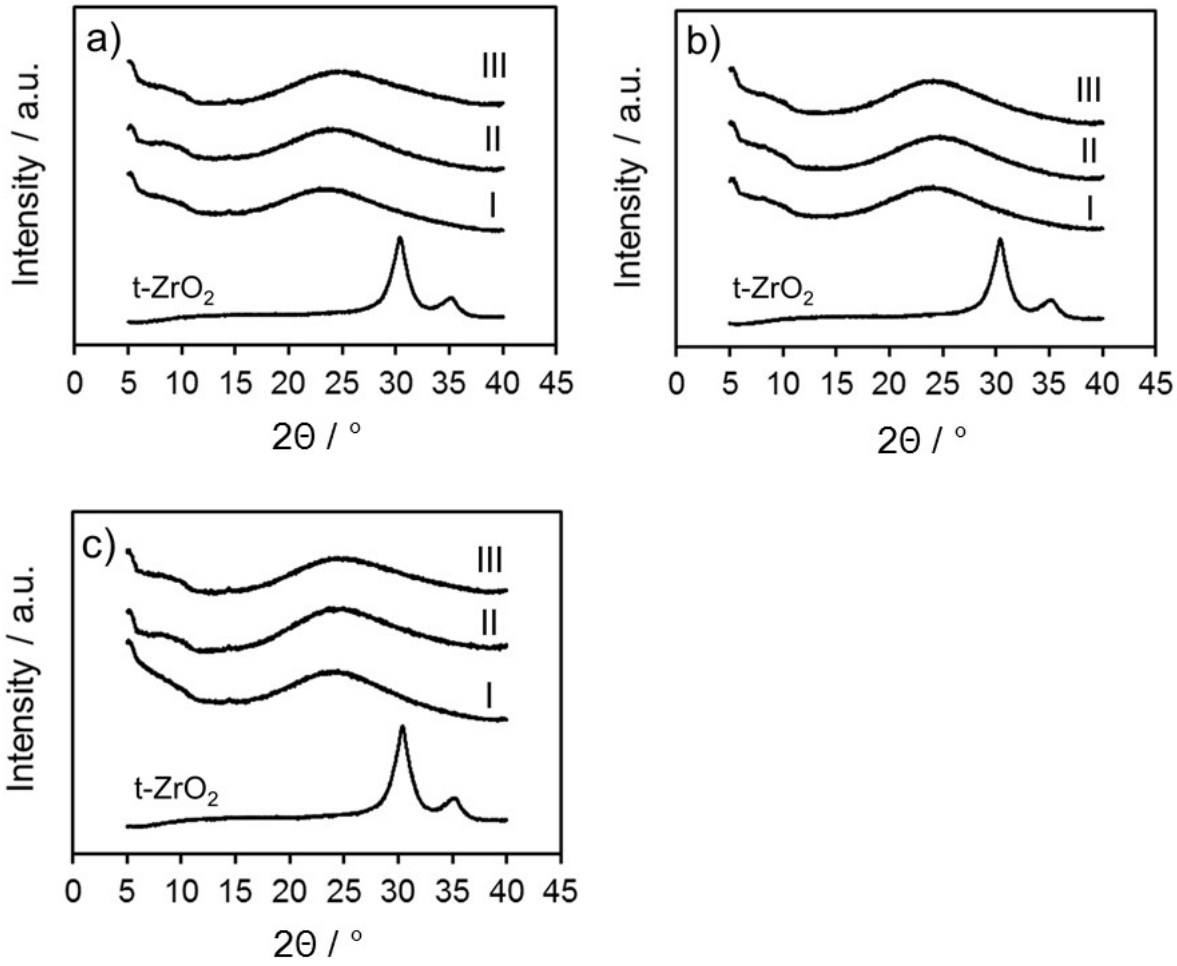


Figure S 6 CO_2 adsorption (circles) and H_2 adsorption (squares) at 35 °C (filled symbols) and 70 °C (unfilled symbols) of butanol SiO_2 spheres.

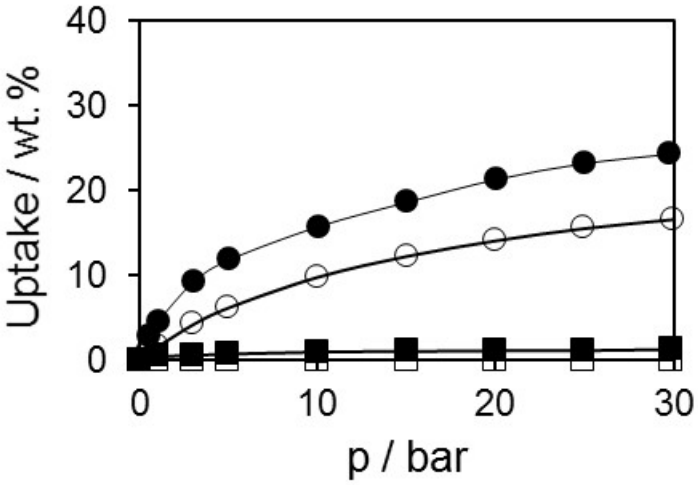
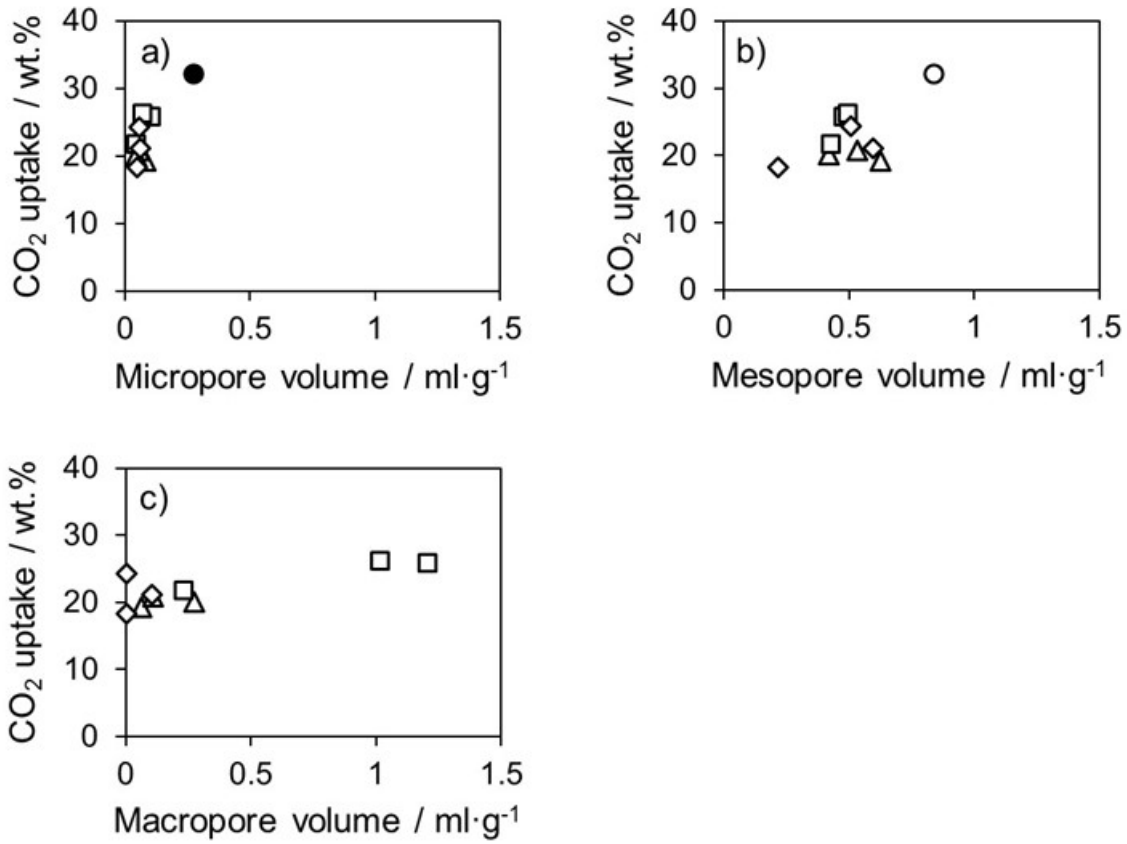


Figure S 7 Correlation between CO_2 uptake (35 °C, 40 bar) and (a) micropore, (b) mesopore and (c) macropore volume. SBA-15 (non-filled circle), zeolite 13X (filled circle) and aniline (triangle), benzyl alcohol (diamond) and butanol (square) spheres with varying Zr^{4+} contents.



Supporting tables

Table S 1 C, H, N and Zr elemental analysis of aniline, benzyl alcohol and butanol spheres.

	C	H	N	Zr
	[wt.%]	[wt.%]	[wt.%]	[wt.%]
As prepared SiO_2 spheres				
Aniline Zr(0)	37.2	5.2	3.4	
Aniline Zr(1)	37.9	5.1	2.4	
Aniline Zr(7)	34.2	4.5	2.5	
Benzyl alcohol Zr(0)	38.4	5.2	2.4	
Benzyl alcohol Zr(1)	39.3	5.2	2.4	
Benzyl alcohol Zr(7)	37.9	5.3	2.4	
Butanol Zr(0)	35.7	4.9	2.1	
Butanol Zr(1)	31.4	4.2	2.4	
Butanol Zr(7)	33.3	4.7	2.12	
Calcined SiO_2 spheres				
Aniline Zr(0)	0.5	1.0	< 0.1	0
Aniline Zr(1)	0.0	1.3	< 0.1	1.17
Aniline Zr(7)	0.5	1.4	< 0.1	6.3
Benzyl alcohol Zr(0)	0.4	1.5	< 0.1	0
Benzyl alcohol Zr(1)	0.3	1.6	< 0.1	1.15
Benzyl alcohol Zr(7)	0.3	1.4	< 0.1	7.2
Butanol Zr(0)	0.0	1.5	< 0.1	0
Butanol Zr(1)	0.1	1.7	< 0.1	1.2
Butanol Zr(7)	0.2	1.4	< 0.1	7.0

Table S 2 BET surface area of aniline, benzyl alcohol and butanol spheres.

	BET surface area [$m^2 \cdot g^{-1}$]
As prepared SiO_2 spheres	
Aniline Zr(0)	35
Aniline Zr(1)	35
Aniline Zr(7)	84
Benzyl alcohol Zr(0)	33
Benzyl alcohol Zr(1)	13
Benzyl alcohol Zr(7)	< 5
Butanol Zr(0)	29
Butanol Zr(1)	69
Butanol Zr(7)	64
Calcined SiO_2 spheres	
Aniline Zr(0)	520
Aniline Zr(1)	507
Aniline Zr(7)	478
Benzyl alcohol Zr(0)	534
Benzyl alcohol Zr(1)	525
Benzyl alcohol Zr(7)	511
Butanol Zr(0)	660
Butanol Zr(1)	610
Butanol Zr(7)	554

Table S 3 Pore volume (N_2 physisorption) of aniline, benzyl alcohol and butanol spheres. (a) Pore size smaller than 2 nm determined by t-plot method, (b) pore size of 2 to 50 nm determined by BJH method (desorption branch).

	Micropore volume[a] [$cm^3 \cdot g^{-1}$]	**Mesopore volume**[b] [$cm^3 \cdot g^{-1}$]
As prepared SiO_2 spheres		
Aniline Zr(0)	0	0.26
Aniline Zr(1)	0	0.19
Aniline Zr(7)	0	0.33
Benzyl alcohol Zr(0)	0	0.26
Benzyl alcohol Zr(1)	0	0.11
Benzyl alcohol Zr(7)	0	0.02
Butanol Zr(0)	0	0.19
Butanol Zr(1)	0	0.32
Butanol Zr(7)	0	0.26
Calcined SiO_2 spheres		
Aniline Zr(0)	0.08	0.54
Aniline Zr(1)	0.06	0.47
Aniline Zr(7)	0.05	0.37
Benzyl alcohol Zr(0)	0.06	0.53
Benzyl alcohol Zr(1)	0.06	0.45
Benzyl alcohol Zr(7)	0.05	0.17
Butanol Zr(0)	0.10	0.38
Butanol Zr(1)	0.07	0.37
Butanol Zr(7)	0.04	0.39

Table S 4 Average pore size (N_2 physisorption) determined by BJH method (desorption branch) of aniline, benzyl alcohol and butanol spheres.

	Average pore size [nm]
As prepared SiO_2 spheres	
Aniline Zr(0)	15
Aniline Zr(1)	15
Aniline Zr(7)	10
Benzyl alcohol Zr(0)	15
Benzyl alcohol Zr(1)	17
Benzyl alcohol Zr(7)	9
Butanol Zr(0)	7.8
Butanol Zr(1)	3.7
Butanol Zr(7)	8.6
Calcined SiO_2 spheres	
Aniline Zr(0)	15
Aniline Zr(1)	3.6
Aniline Zr(7)	3.6
Benzyl alcohol Zr(0)	3.6
Benzyl alcohol Zr(1)	3.6
Benzyl alcohol Zr(7)	3.6
Butanol Zr(0)	3.6
Butanol Zr(1)	3.6
Butanol Zr(7)	3.7

Table S 5 Macropore volume determined by Hg porosimetry of aniline, benzyl alcohol and butanol spheres.

	Macropore volume [$cm^3 \cdot g^{-1}$]
Calcined SiO_2 spheres	
Aniline Zr(0)	0.07
Aniline Zr(1)	0.11
Aniline Zr(7)	0.27
Benzyl alcohol Zr(0)	0.11
Benzyl alcohol Zr(1)	0.00
Benzyl alcohol Zr(7)	0.00
Butanol Zr(0)	1.21
Butanol Zr(1)	1.02
Butanol Zr(7)	0.23

Table S 6 Integrated areas of the IR peaks (absorbance) at equilibrium conditions of 10 mbar CO_2.

	Approximated wavenumber [cm^{-1}]				
	1633	1610	1500	1458	1380
Aniline Zr(0)	0.65				
Aniline Zr(7)		3.52	1.03	0.58	0.16
Benzyl alcohol Zr(0)	0.69				
Benzyl alcohol Zr(7)		5.79	3.40	0.54	0.39
Butanol Zr(0)	1.31				
Butanol Zr(7)		5.21	1.12	0.37	0.11

Table S 7 Standard heat of adsorption (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) of the adsorption of CO_2 obtained by the Langmuir adsorption model.

	CO_2	
	ΔH^0_{ads} [kJ·mol^{-1}]	ΔS^0_{ads} [J·mol^{-1}·K^{-1}]
SBA-15	- 8.6	- 55.5
13X	- 29.5	- 86.0
Aniline Zr(0)	- 9.3	- 47.7
Aniline Zr(1)	- 12.3	- 56.9
Aniline Zr(7)	- 15.4	- 69.3
Benzyl alcohol Zr(0)	- 12.3	- 56.8
Benzyl alcohol Zr(1)	- 16.8	- 71.6
Benzyl alcohol Zr(7)	- 7.7	- 43.9
Butanol Zr(0)	- 17.6	- 74.2
Butanol Zr(1)	- 16.0	- 68.8
Butanol Zr(7)	- 13.3	- 62.9